hydrogen allotropes and isotopes by degassed alumina.[14] Indeed, the estimate of the surface field given above for zinc oxide is of the same order as estimates made by different techniques for adsorbed hydrogen on alumina.[14,15] Further studies aimed at more fully characterizing this weak hydrogen chemisorption are underway.

Acknowledgment. This work was aided by funds from the NSF under Grant No. GP-22830.

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(15) F. H. Van Cauwelaert and W. K. Hall, presented at the Second North American Meeting of The Catalysis Society, Houston, Tex., Feb 24-26, 1971.

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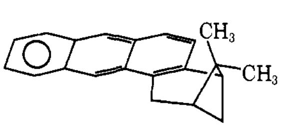
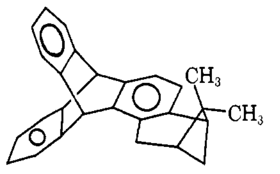
Anomalous Preferential Addition of Dienophiles to the Hindered Face of Apopinanthracene[1]

Sir:

Apopinanthracene[2] (ApAn) is an unusual aromatic hydrocarbon that does not have a symmetry plane by virtue of *gem*-dimethyl groups at C_3. Consequently it has two faces, β (front) and α (back), relative to the *gem*-dimethyl group.[3] Two sharp signals (40 and 88 Hz, 3 H each) are observed in the alkyl region which correspond to the *syn*- (shielded) and *anti*-C_3Me groups, respectively. In the corresponding triptycene, **1** (mp 223–225°, from ApAn and benzyne), both the *syn*- and *anti*-C_3Me resonances are shifted further upfield (to 30 and 79 Hz, respectively) as a result of increased shielding by the angular aromatic ring.



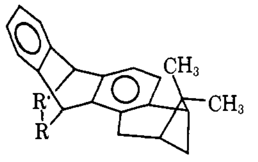
ApAn



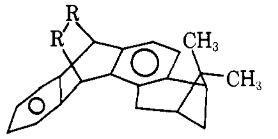
1

The reaction of ApAn with other dienophiles should in principle lead to two kinds of adducts as a result of frontside (β) and backside (α) attack. *A priori* backside attack (α) would be expected to predominate from steric considerations.

A mixture of Diels–Alder adducts, **2**, was prepared from ApAn and dimethyl acetylenedicarboxylate (DMAD). Pmr analysis, utilizing the relative area of the two *syn*-C_3Me signals at 29 (33%) and 36 Hz (67%), was used to determine the amount of each adduct. The signal at 29 Hz was assigned to **2**α, since the juxtaposition of the angular aromatic ring and the *syn*-C_3Me group in this isomer is almost identical with that in apopinotriptycene (**1**), and that at 36 Hz was assigned to **2**β. Unexpectedly, there is a preference by a factor of two (67:33) for [4 + 2] cycloaddition to the "wrong" (more hindered) side.



α



β

2(α, β), R–R = MeO_2CCCCO_2Me

3(α, β), R–R = $(NC)_2C$–$C(CN)_2$

4(α, β), R–R = o-F_4C_6<

5(α, β), R–R = O–O

Consequently, the reaction of ApAn with various dienophiles [tetracyanoethylene (TCNE), tetrafluorobenzyne (TFB), and singlet oxygen ($^1O_2$)] was undertaken in order to determine the generality of this phenomenon (Table I). The reaction products were analyzed by pmr and structural assignments were made in accordance with the aforementioned reasoning. In all cases the major isomer (60–70%) was formed by addition to the β (more hindered) face of ApAn.

Table I. Ratio of Diels–Alder Adducts from ApAn and Various Dienophiles

Dienophile	Adduct(s)[a]	Chemical shift, Hz (rel area) *syn*-C_3Me	*anti*-C_3Me	β/α addition
Benzyne[b]	**1**	30 (1)	78 (1)	
DMAD[c]	**2**α **2**β	29 (0.33) 36 (0.67)	80 81 (1)	2
TCNE[c]	**3**α **3**β	29 (0.40) 43 (0.60)	86 87 (1)	1.5
TFB[d]	**4**α **4**β	30 (0.35) 39 (0.65)	79 (0.38) 87 (0.62)	1.9
$^1O_2$[e]	**5**α **5**β	28 (0.33) 40 (0.67)	80 (0.33) 82 (0.67)	2

[a] Product composition independent of reaction conditions. [b] Generated from benzenediazonium 2-carboxylate in 1,2-dichloroethane. [c] Reaction effected in dioxane or carbon tetrachloride. [d] Generated from bromopentafluorobenzene and magnesium in THF. [e] Reaction effected in CS_2 using Rose Bengal as the sensitizer.

With maleic anhydride (MA), all four possible Diels–Alder adducts were obtained[4]—*syn*-**6**β (38 Hz), *anti*-**6**β (34 Hz), *syn*-**6**α (31 Hz), and *anti*-**6**α (28 Hz). The ratio of β to α attack, *i.e.*, (*syn*- + *anti*-**6**β)/(*syn*- + *anti*-**6**α) was ~1 instead of 2.

The lower β/α ratio (1:1) for the ApAn–MA reaction is probably a consequence of lower reactivity of

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(1) Taken in part from the Ph.D. Thesis of J. G. M., Case Western Reserve University, 1971.

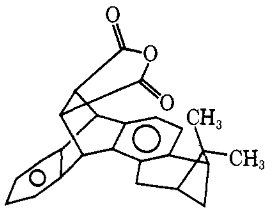
(2) (−)-3,3-Dimethyl-2,4-methano-1,2,3,4-tetrahydrobenz[*a*]anthracene, mp 102–103°, $[\alpha]^{25}D$ −149° (*c* 2, EtOH); 93% optically pure. All new compounds (except for **5**, unstable) gave analyses consistent with assigned chemical composition. Complete physical, spectral, and optical characterization will be reported in the full paper.

(3) *Cf.* steroid nomenclature conventions.

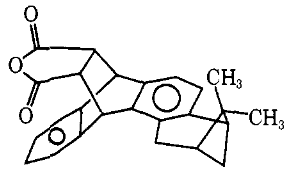
(4) Based on the *syn*-C_3Me resonances. These assignments received further support from the results obtained by adding 1,3,5-trinitrobenzene (TNB) to a solution of *syn*- and *anti*-**6**α and -**6**β in CCl_4 or $DCCl_3$. All of the *syn*-C_3Me group signals are affected in the order *anti*-**6**α ~ *syn*-**6**α > *anti*-**6**β >>> *syn*-**6**β.[5] With the addition of incremental amounts of TNB the *syn*-C_3Me resonance of *syn*-**6**α coalesces with *anti*-**6**α (31 → 28 Hz). Further addition causes *anti*-**6**β to coalesce with this (34 → 28 Hz). The *syn*-C_3Me signal of *anti*-**6**α was essentially unaffected (ΔHz ~ 1.0). This phenomenon can be reversed by the addition of a better acceptor (*e.g.*, ApAn[6] or 2-*tert*-butylanthracene) than **6**.

(5) The magnitude of ΔHz is related to the ability of the TNB to "affect" the environment of the *syn*-C_3Me group.

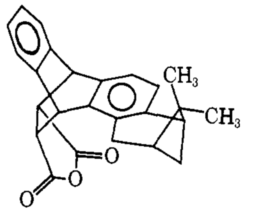
(6) ApAn and TNB form a blood-red charge-transfer complex. TNB and **6** apparently do not.



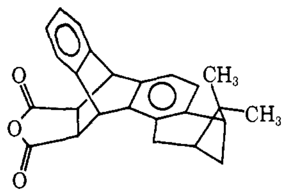
syn-**6β**, 19%



anti-**6β**, 30%



syn-**6α**, 39%



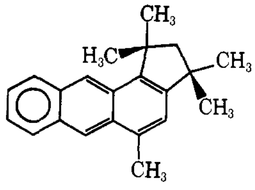
anti-**6α**, 12%

MA, hence greater susceptibility to steric factors (*cf.* the amount of *syn*-**6β**). The greater reactivity of the β face, however, is best reflected by comparing *anti*-**6β** (30%) to *anti*-**6α** (12%). Thus, with *most* dienophiles ApAn reacts preferentially from the *more hindered* side.

Why this preference? The only apparent difference is the presence of the *gem*-dimethyl group. Thus, an explanation for preferred attack on the more congested β side is that it is more nucleophilic to electrophiles such as DMAD, TCNE, $^1O_2$, TFB, and MA irrespective of steric factors.[7]

If indeed the β face of ApAn is more nucleophilic than the α face, the presence of a π-complexing agent[6] might alter the product distribution by preferentially complexing to the β face. This was shown to be erroneous, since in reactions of ApAn with MA and DMAD the only effect of 10 equiv of TNB was to decrease the reaction rate.[9] These results also rule out a solvent-related entropy effect.

While ApAn is only 1.2 times more reactive than anthracene as a benzyne scavenger, with MA (80°, CCl_4) it is 34 times[10] more reactive than anthracene, and 7.5 times more reactive than 2-*tert*-butyl-[11] and 1,2-dimethylanthracene. Only the trisubstituted anthracene **7** approaches the Diels–Alder reactivity of ApAn.[12]



7

From these preliminary results there is little doubt that ApAn, as a consequence of its structure, has chemically nonequivalent aromatic faces which we attribute to σ–π orbital overlap of the *syn*-C_3Me or *gem*-dimethyl groups with the aromatic π system. Its increased Diels–Alder reactivity may also be a result of this and/or overlap with the strained rigid cyclobutane ring.

Other manifestations of this facial nonequivalence (π-orbital distortion) are under investigation.

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[7] This may be a result of secondary orbital overlap between the σ-bonding electrons of the *gem*-dimethyl group and the π-bonding electrons within the aromatic periphery. Partial support for this idea exists: (1) ApAn, $\lambda_{\max}$ 265 nm; anthracene, $\lambda_{\max}$ 254 nm; *i.e.*, a bathochromic shift of 11 nm which also is observed with a wide variety of polycyclic apopinarenes and their corresponding parents; (2) MA and 2-substituted anthracenes give syn and anti adducts in ratios that agree with the conclusion that the transition state containing the MA fragment above the more electron-rich aromatic ring is more stable than the other possibility [F. Kaplan and H. Conroy, *J. Org. Chem.*, **28**, 1593 (1963)]. The *syn*-**6α**/*anti*-**6α** ratio (3.3:1) further supports this contention. The lower *syn*-**6β**/*anti*-**6β** ratio (2:3) can be attributed to steric interactions.[8]

[8] The thermal equilibration (syn–anti adduct isomerization) of maleic anhydride–anthracene adducts will be reported upon separately.

[9] *Cf.* B. H. Klanderman and T. R. Criswell, *J. Amer. Chem. Soc.*, **91**, 510 (1969), for related observations with benzyne and substituted anthracenes.

[10] (a) Lack of selectivity of benzyne relative to MA is well documented (D. M. Smith, Ph.D. Thesis, Case Western Reserve University, 1972). (b) At 80° the relative rates are: anthracene, 1.00; 1-Me, 0.84; 2-Me, 1.06.

[11] These D-A isomers are easily separated: syn, mp 216°; anti, mp 274°.

[12] Kinetic runs were conveniently made in the pmr probe in 1.0 ml of solvent containing 0.3 mmol of the anthracene and 1–10 equiv of dienophile. This technique will be reported in detail elsewhere.

The Degenerate Thermal Rearrangement of *cis*-9,10-Dihydronaphthalene[1]

Sir:

Perhaps owing to its propensity for disproportionation[2] and to its rather unflattering position as the "thermodynamic sink" on the thermal energy surface which interrelates a large number of $(CH)_{10}$ structural isomers,[2b,3] *cis*-9,10-dihydronaphthalene (**1**) has not held the degree of sustained fascination one normally anticipates for interesting molecules. Another major source of disappointment in the brief history of **1** is the early report by van Tamelen and Pappas[4] that this polyene exhibits "no overt tendency for cyclodecapentaene formation." Notwithstanding, certain theoretical considerations having their basis in orbital symmetry[5] have led us to investigate the possibility that the *cis*-9,10-dihydronaphthalene molecule (**1**) might be capable of degenerate skeletal rearrangment under conditions of thermal activation. Fundamentally at issue was the question of whether one or more of several possible carbon scrambling mechanisms (see below) were occurring at a kinetic level competitive with disproportionation schemes or with other symmetry-allowed but degeneracy-destroying reactions such as stereospecific [1,5] sigmatropic hydrogen shifts. A study of this

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[1] Support of this work by the National Science Foundation and the National Cancer Institute is gratefully acknowledged.

[2] (a) W. von E. Doering and J. W. Rosenthal, *J. Amer. Chem. Soc.*, **89**, 4534 (1967); (b) L. A. Paquette and J. C. Stowell, *ibid.*, **93**, 2459 (1971).

[3] (a) W. von E. Doering and J. W. Rosenthal, *ibid.*, **88**, 2078 (1966); M. Jones, Jr., and L. T. Scott, *ibid.*, **89**, 150 (1967); (c) M. Jones, Jr., *ibid.*, **89**, 4236 (1967); (d) E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967); (e) W. von E. Doering and J. W. Rosenthal, *Tetrahedron Lett.*, 349 (1967); (f) M. Jones, Jr., and B. Fairless, *ibid.*, 4881 (1968); (g) S. Masamune, R. T. Seidner, H. Zenda, M. Weisel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, **90**, 5286 (1968); (h) S. Masamune and R. T. Seidner, *Chem. Commun.*, 542 (1969); (i) R. T. Seidner, N. Nakatsuka, and S. Masamune, *Can. J. Chem.*, **48**, 187 (1970); (j) M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, **92**, 3118 (1970); (k) E. E. van Tamelen and R. H. Greeley, *Chem. Commun.*, 601 (1971).

[4] E. E. van Tamelen and B. Pappas, *J. Amer. Chem. Soc.*, **85**, 3296 (1963).

[5] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **91**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).